Agricultural Pesticide Residues in Oysters and Water from Two Chesapeake Bay Tributaries

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Little is known of the impact of agricultural activity on oysters in Chesapeake Bay tributaries. As a preliminary assessment of pesticide residues in oyster tissues, this study monitored more than 60 pesticides in oysters and overlying water in two tributaries of the Chesapeake Bay. Paired water and oyster samples were collected throughout 1997 from the Patuxent and Choptank Rivers which discharge into opposite shores of the Chesapeake Bay in Maryland. In water, herbicides such as atrazine, simazine, cyanazine, and metolachlor were present throughout the year with individual water concentrations peaking as high as 430 ng/l in the late spring and summer and subsiding in the fall. These herbicides were not detected in the oysters even when concentrations were highest in the water. Another herbicide, trifluralin, was detected throughout the year at concentrations of less than 0.6 ng/l and 0.4 ng/g (wet weight) in water and oyster samples, respectively. Several insecticides, such as endosulfans I and II, endosulfan sulfate, chlorpyrifos, α- and γ-HCH, p,p'-DDE, o,p'-DDT, *trans*-nonachlor, and *trans*-chlordane were also measured in both oysters and water at low concentrations. Published by Elsevier Science Ltd

Introduction

The Mussel Watch Project (MWP), currently administered by the National Oceanic and Atmospheric Administration (NOAA) National Status and Trends (NS and T) Program, has monitored environmental contaminants in shellfish in U.S. coastal waters since the 1970s (Lauenstein, 1995; O'Connor, 1991). The project involves annual sampling of oysters and other mollusks at selected sites along the U.S. coasts, and analyzing the samples for metals and organic pollutants such as polychlorinated biphenyls (PCB), polycyclic aromatic hydrocarbons (PAH), and several organochlorine (OC) pesticides (Lauenstein and Cantillo, 1993). The oysters serve as biomonitors

of environmental quality to help determine the trends, persistence, and fate of pollutants as well as the environmental, ecological, and other consequences of pollution. An additional reason to monitor contaminants in oysters and other seafood relates to the gathering of human exposure information for risk assessment and setting regulatory tolerances.

Many of the MWP target contaminants, such as DDT, were banned from use in the U.S. in the 1970s. Despite the continued need to monitor these persistent and toxic contaminants in the environment, there is also a need to monitor for many current use pesticides. Of the hundreds of insecticides and herbicides that are registered in the U.S. for applications in agriculture (EPA, 1997), the MWP only monitors a few currently registered pesticides including lindane, chlorpyrifos, endosulfan I and endosulfan II (Cantillo et al., 1997). Also, the timing of sample collection for the MWP, generally in the winter, does not coincide with peak usage of many potential pesticide contaminants in the Chesapeake Bay watershed (Lauenstein and Cantillo, 1993).

This project was designed as a preliminary study to determine the concentrations of a wide range of currently used pesticides in oysters and overlying water before, during, and after the agricultural season in the Chesapeake Bay region. This study is the first to monitor for these currently used pesticides in Chesapeake Bay oysters. However, several studies have examined water concentrations of these chemicals in the surface water of the Chesapeake Bay watershed. Glotfelty et al. (1984) conducted a three year investigation of the Wye River estuary on the eastern shore of the Chesapeake Bay to determine the most important factors influencing pesticide run-off of the herbicides atrazine and simazine. Foster and Lippa (1993) determined annual riverine loadings of several banned and currently used pesticides entering the Chesapeake Bay from the Potomac, James, and Susquehanna Rivers. McConnell et al. (1997) measured chlorpyrifos concentrations in surface water and in air over the Chesapeake Bay mainstem during the spring, summer, and

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fall of 1993 to determine temporal and spatial trends and to discern the interaction between the atmosphere and surface waters with respect to the fate and transport of pesticides. Harman (1996) monitored 13 important agricultural herbicides and insecticides during the spring of 1994 and 1995 in the surface water, air, and rain of the Patuxent River estuary to determine spatial and temporal trends in water concentrations and the atmospheric loadings of pesticides to the watershed. The choice of the Patuxent River and inclusion of the same pesticides in this study provided continuity in the water data and further help to evaluate the effects of agricultural practices in the region.

One key element missing from previous studies of pesticide fate in the Chesapeake Bay surface waters is their accumulation by biota. Because oysters filter a large amount of water during their feeding process, and because they are easy to collect, oysters are an excellent study organism for monitoring the potential bioaccumulation of chemicals present in the water. By measuring the pesticide concentrations in the oysters and surrounding water collected at the same time, over the course of time, the distribution of the pesticides between the biota and water may be ascertained. Oysters may take several weeks to reach an equilibrium with a constant pesticide concentration in the water (Serrano et al., 1997). Furthermore, by collecting samples from two sites, results may be compiled and compared. The results from this work will help increase our understanding of the influence of agricultural activity on aquatic species of the Chesapeake Bay and elsewhere.

Materials and Methods

Target pesticides

Table 1 lists the pesticides targeted in this study categorized by class. Several of the herbicides (triazines/tetrazines and amides/anilides and others) were selected due to known occurrences from previous studies (Harman, 1996) or due to high usage rates in the area. Several OC insecticides were included for analysis due to their known occurrence in oysters (NOAA, 1995). Other pesticides, mainly organophosphate insecticides, were added on the basis of EPA priorities as presented to the Pesticide Data Program (USDA, 1997) and their prevalence of use in agriculture and/or households. Organic chemical contaminants other than pesticides were beyond the scope of this project and were not analyzed. In all, 60 pesticides were included for determination in all sample extracts including fortified samples. Another set of 63 pesticides, for a total of 123, were spot-checked in many of the chromatograms at known retention times and characteristic mass spectra. Recoveries and detection limits were not determined for the additional compounds, and they were assumed to be similar to those of closely related compounds used in the spiking study (Fillion et al., 1995).

Sampling

Two sampling sites in tributaries of the Chesapeake Bay in Maryland were selected for the study (Fig. 1). The Patuxent River, on the western shore, is the largest river located entirely within the state of Maryland. It runs through agricultural, urban, and suburban areas before reaching the bay. The sampling site in the Patuxent River (38° 23′ 37″ N, 76° 33′ 25″ W) is located at the Gatton oyster bar situated ≈ 20 km upstream from the mouth of the river. The Choptank River on the eastern shore mainly runs through agricultural and rural land, and the area contains very productive oyster bars and a successful oyster hatchery. The Choptank River sampling site was located mid-river at the Sandy Hill oyster bar (38° 35′ 57″ N, 76° 06′ 51″ W). The depth of both oyster bars was approximately 5.5 m. Both sites were also chosen due to their proximity to research stations on the shore and the analytical laboratory in Beltsville. The Choptank River site is the same as an existing MWP site, and the Patuxent River site is approximately 20 km upstream from the MWP site at Hog Point, which is useful for comparison of the analytical results between these sites.

As shown in Table 2, oyster and water samples were collected on monthly, bi-weekly, or weekly intervals from 13 February through 12 November 1997 from the Patuxent River site, and 27 May through 11 November 1997 from the Choptank River site. Sample collections were performed weekly during the late spring when the highest pesticide levels were expected to occur in the water, and sampling was conducted less frequently during other times of the year. Herbicide concentrations are also known to increase in river water on the days following storm events due to run-off (Glotfelty et al., 1984; Harman, 1996), and sampling dates that followed appreciable rainfalls (> 1 cm) are noted in Table 2. Table 2 also contains data on river salinity, and temperature at the time of sampling which were obtained by direct measurement and/or from the University of Maryland's monitoring buoys. Rain data was provided by the University of Maryland's Department of Meteorology.

Oyster samples were collected by dredging, and the 10–12 selected adult oysters (*Crassostrea virginica*), larger than 3.5 inches, were immediately scrubbed, rinsed with water, and shucked. Each oyster sample was fortified with deuterated phenanthrene (d_{10}-phenanthrene) solution, homogenized, and stored at $-20°C$ until they were analyzed in December 1997. The percent moisture of the samples was measured by freeze-drying one of the portions soon after collection or oven-drying ≈ 15 g portions at the time of analysis.

Water samples were taken from a depth of 3.7 m over the area where the oysters were collected and

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stored in an 18 l stainless steel canister for transport to the laboratory. The canister was pressurized in the laboratory with N_2 to force the water through a 1 µm pore size GMF-150 graded density glass fiber filter followed by a 0.7 µm pore size, GF/F glass fiber filter (Whatman; Maidstone, UK). On the same day as collection, the filtered sample was fortified with 50 µl of 74.5 ng/µl d_{10}-phenanthrene and/or 20 ng/µl d_{10}-diazinon and extracted.

Sample extraction and analysis

Solid-phase extraction (SPE) with polymer-based ENV+ (Isolute; Mid Glamorgan, UK) cartridges was used for extraction of the water samples. For oysters, tissue was blended with acetonitrile and a series of SPE cartridges (primary secondary amine, alumina-neutral, and graphitized carbon) were used for clean-up. Gas

chromatographic (GC) analysis of the water and oyster extracts was performed using ion-trap mass spectrometric detection (ITMS) for all target pesticides and negative chemical ionization mass spectrometric detection (NCI-MS) on a quadrupole instrument in selective ion monitoring (SIM) mode to obtain lower detection limits of several halogenated pesticides. More detailed descriptions of the analytical methods will be presented separately. Appropriate quality control measures were performed to ensure the validity of analytical results.

The limits of detection (LOD) are the average concentrations at which the signal/noise ratios equaled 3 for the pesticides fortified in the different matrices. The LOD for oyster samples was <5 ng/g (wet weight) and <5 ng/l for water samples. For water samples, recoveries ranged from 87 to 116% with only three outlying low recoveries of 55, 66, and 75% for esfen-

TABLE 1

Pesticides and related analytes monitored in the oyster and water samples.

Organophosphates	*Organochlorines*	*Amides/Anilides*
acephate[a]	aldrin[a]	acetochlor
azinphos-methyl	cis-chlordane	alachlor
carbofenothion[a]	trans-chlordane[a]	allidochlor[a]
chlorfenvinphos[a]	chlorothalonil	butachlor[a]
chlorpyrifos	p,p'-DDE	metolachlor
chlorpyrifos-methyl[a]	o,p'-DDE[a]	pronamide[a]
chlorpyrifos oxon[a]	p,p'-DDD	propachlor[a]
coumaphos[a]	o,p'-DDD[a]	propanil[a]
demeton-S-sulfone[a]	p,p'-DDT	
diazinon	o,p'-DDT[a]	*Triazines/Tetrazines*
dichlorvos	dicofol	ametryn[a]
dimethoate	dichlorobenzophenone[a]	atrazine
disulfoton[a]	dieldrin	CEAT[a] (atrazine degradant)
disulfoton sulfone[a]	endosulfan I	CIAT (atrazine degradant)
ethoprop	endosulfan II	cyanazine
ethion	endosulfan sulfate	metribuzin
fenamiphos[a]	endrin	prometon[a]
fenamiphos sulfone[a]	heptachlor	propazine[a]
fenamiphos sulfoxide[a]	heptachlor epoxide	simazine
fenthion[a]	hexachlorobenzene	
malathion	α-HCH[a]	*Others*
methamidophos[a]	β-HCH[a]	buprofezin
methidathion	γ-HCH (lindane)	captan[a]
mevinphos[a]	δ-HCH[a]	dacthal
omethoate[a]	o,p'-methoxychlor[a]	dicloran
oxydemeton methyl sulfone[a]	p,p'-methoxychlor	diphenylamine[a]
parathion	methoxychlor olefin[a]	diuron[a]
parathion-methyl	mirex	ethalfluralin[a]
phorate[a]	trans-nonachlor	imazalil[a]
phorate sulfone[a]	oxychlordane[a]	iprodione
phorate sulfoxide[a]	pentachloroanisole	linuron[a]
phosalone	pentachlorobenzene	metalaxyl[a]
phosmet	pentachloronitrobenzene	myclobutanil
phosphamidon[a]	tetrachloronitrobenzene[a]	oxyfluorfen[a]
sulprofos[a]		pendimethalin
terbufos	*Pyrethroids*	o-phenylphenol[a]
terbufos sulfone[a]	bifenthrin[a]	piperonyl butoxide[a]
tetrachlorvinphos	cyfluthrin[a]	propargite[a]
	cypermethrin[a]	tetrahydrophthalimide[a]
Carbamates	esfenvalerate	thiabendazole[a]
butylate	fenvalerate	trifluralin
carbaryl	cis-permethrin	vinclozolin
carbofuran	trans-permethrin	
chlorpropham[a]		
propoxur		
vernolate		

[a]Monitored in extracts, but not included in spiking solution.

valerate, chlorothalonil, and dichlorvos, respectively. For oyster samples, recoveries ranged from 84 to 120% with outlying values of 20, 39, 42, 44, 56, 139, and 156% for dichlorvos, CIAT, chlorothalonil, hexachlorobenzene, iprodione, endosulfan sulfate, and azinphosmethyl, respectively. The reagent blanks did not contain any detectable levels of pesticides.

Results and Discussion

Water results

Table 3 and Table 4 list the analytical results for the water samples by date (month/day) collected in 1997

from the Patuxent and Choptank Rivers. All water results correspond to the dissolved phase only, and results for particulate matter will be presented separately. The values in the tables are the average concentration of duplicate samples for GC/ITMS results, or single measurement determinations for GC/NCI-MS. The precision of the duplicate measurements in GC/ITMS was very good, generally <10% difference, and agreement was excellent in those cases when a pesticide could be quantified in both GC/ITMS and GC/NCI-MS.

A total of 18 different analytes were detected in the water samples with the same ones found in both rivers
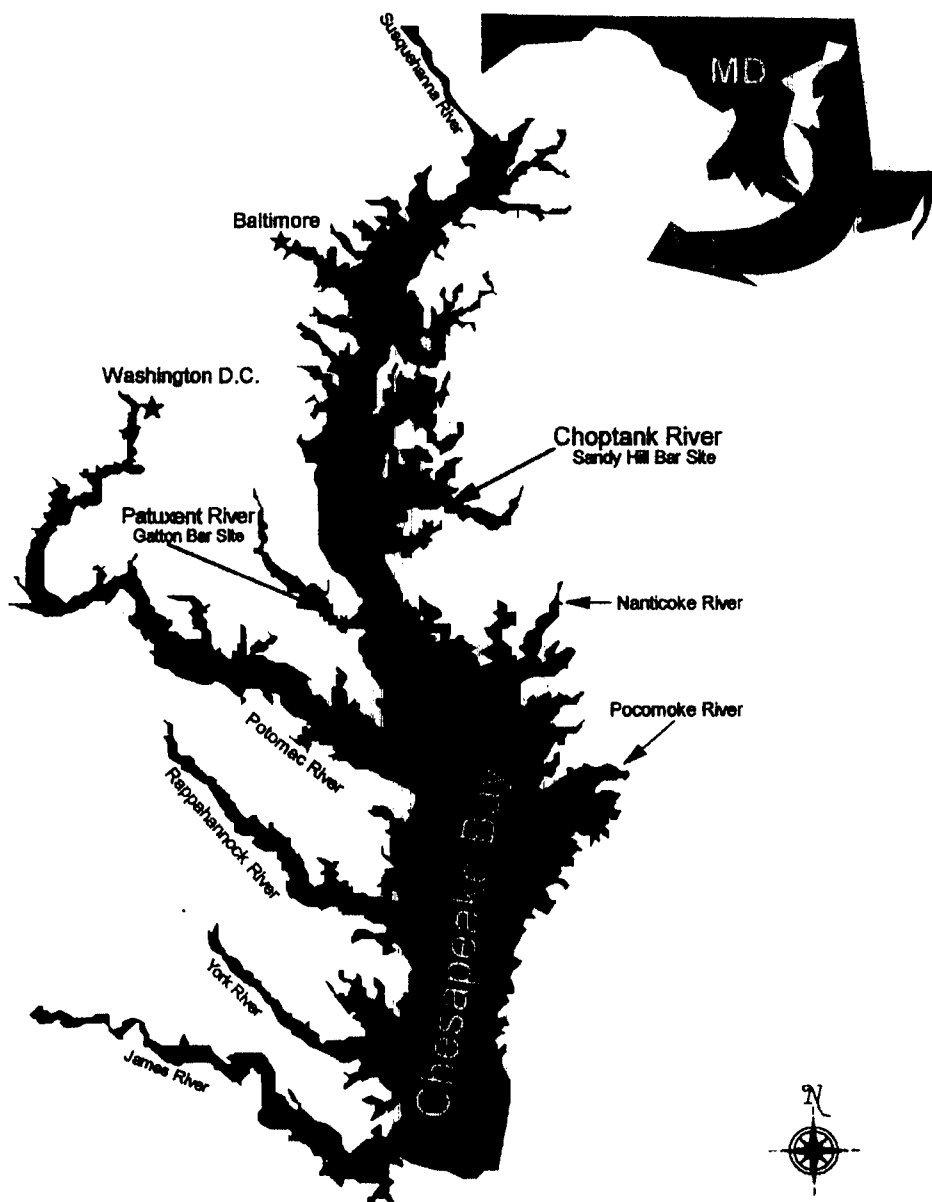

Fig. 1 Map of the Chesapeake Bay in which the sampling sites on the Patuxent and Choptank Rivers are noted.

TABLE 2

Sampling dates in 1997 on the Patuxent and Choptank Rivers, temperature, and salinity of the water, and percent moisture of the oyster samples.

	Patuxent River				Choptank River		
Date	Temp. (°C)	Salinity ‰	% H₂O in oysters	Date	Temp. (°C)	Salinity ‰	%H₂O in oysters
Feb. 13	3.2	7.2	88.5				
March 13	8.3	7.8	88.7				
April 14[a]	11.6	7.2	87.1				
April 22	12.1	7.4	87.5				
April 29[a]	13.2	7.5	87.2				
May 8	15.7	8.0	85.9				
May 15	17.1	8.2	86.9				
May 22	17.4	9.3	84.1				
May 28[a]	18.5	9.0	82.3	May 27	18.3	8.1	87.3
June 4[a]	18.0	9.0	87.6	June 6[a]	18.0	8.2	87.3
June 11	22.0	8.3	87.6	June 10	21.4	8.0	88.2
June 18	18.1	9.6	86.9	June 19	22.5	8.5	87.8
June 24	26.0	8.9	82.0	June 25	26.2	8.6	87.6
July 1	25.6	8.5	83.5	July 2	26.0	8.6	88.6
July 15	28.8	11.3	89.0	July 17	29.0	9.1	88.8
July 30[a]	26.5	11.0	88.8	July 29	27.2	10.3	89.0
Aug. 14	27.0	12.3	90.6	Aug. 12	26.3	11.7	90.9
Aug. 26[a]	24.8	12.6	90.2	Aug. 27	25.0	10.8	90.7
Sep. 10	24.3	13.4	88.9	Sep. 9	28.3	11.5	89.7
Oct. 14	21.3	15.1	89.4	Oct. 16	18.7	13.6	85.2
Nov. 12[a]	12.4	14.5	86.5	Nov. 11[a]	11.6	13.7	86.9

[a]Significant rain event (> 1 cm) occurred within 3 days prior to sampling.

except for p,p'-DDE, which exceeded the LOD in some of the Patuxent River samples, and pendimethalin, which was found in one Choptank River sample. Metolachlor, simazine, cyanazine, and atrazine and one of its major degradation products, CIAT, were observed previously in the Patuxent River (Harman, 1996) and continued to be prevalent in river waters. These herbicides are used extensively in corn and soybean production, which comprise the predominant agricultural crops in the region (Pait et al., 1992). Although essentially the same herbicides and insecticides were found in both rivers, the concentrations were substantially different. Herbicides in the Choptank River were approximately 4 times more concentrated than in the Patuxent River, whereas insecticides such as chlorpyrifos, endosulfan I and endosulfan II occurred at higher levels in the Patuxent samples.

TABLE 3

Concentrations of pesticides in water samples (ng/l) collected on the listed dates in 1997 and the overall averages ± standard deviations (SD) from the Patuxent River site.

Pesticide	2/13	3/13	4/14	4/22	4/29	5/8	5/15	5/22	5/29	6/4	6/11	6/18	6/24	7/1	7/15	7/30	8/14	8/26	9/10	10/14	11/12	Average ±SD
Atrazine[b]	28	54	49	40	40	53	46	44	43	36	56	78	59	69	69	56	49	48	26	19	25	47±15
CIAT[b]	17	53	47	42	36	56	49	43	44	34	36	26	33	24	30	29	23	22	20	10	21	33±13
trans-chlordane[a]	0.52	0.29	0.28	0.26	0.24	0.28	0.44	0.28	0.30	0.27	0.28	0.41	0.30	0.27	0.24	0.30	0.28	0.39	0.33	0.26	0.40	0.31±0.07
Chlorothalonil[a]	ND	0.70	0.06	ND	ND	0.25	0.53	0.42	ND	0.39	0.36	ND	ND	0.25	0.32	159	1.9	1.5	22	ND	ND	0.4±0.2[c]
Chlorpyrifos[a]	NQ	NQ	2.6	3.1	1.7	2.7	2.4	2.1	2.0	1.1	1.1	0.82	2.4	0.91	0.83	1.0	0.92	0.83	1.1	0.76	0.84	1.5±0.8[c]
Cyanazine[b]	ND	ND	89	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	16	18	ND	35	1.4	ND	ND	variable
p,p'-DDE[a]	NQ	2.1	ND	ND	ND	ND	1.7	1.4	1.8	1.8	ND	1.1	0.99	ND	ND	1.6	ND	ND	ND	ND	ND	1.6±0.4[c]
Diazinon[a]	3.1	4.2	3.4	3.8	2.1	3.2	ND	3.2	ND	ND	ND	ND	56	5.1	3.6	1.9	ND	ND	ND	ND	2.6	3.3±0.9[c]
Endosulfan I[a]	NQ	NQ	1.2	1.7	0.58	0.80	0.78	0.83	0.56	0.93	0.64	0.49	0.63	0.51	0.57	0.75	0.68	1.4	5.6	0.49	0.52	0.8±0.3[c]
Endosulfan II[a]	NQ	NQ	2.6	2.3	0.66	1.8	1.3	1.0	0.60	1.0	0.51	0.29	0.88	0.34	0.36	0.76	0.50	2.8	35	0.40	0.37	1.0±0.8[c]
Endosulfan sulfate[a]	NQ	NQ	1.4	0.99	0.36	0.85	0.62	0.54	0.28	0.65	0.38	0.18	0.44	0.19	0.26	0.49	0.31	0.97	4.0	0.19	0.26	0.5±0.3[c]
α-HCH[a]	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	—
γ-HCH[a]	NQ	NQ	2.0	0.84	0.44	0.51	0.59	0.43	0.41	0.51	0.77	0.33	0.41	0.28	0.43	0.45	1.8	0.21	0.24	0.29	0.45	0.6±0.5[c]
Metolachlor[b]	10	22	16	16	16	11	10	8.7	7.8	6.8	11	6.2	19	4.1	2.9	1.1	0.4	1.3	2.5	ND	3.1	9±6[c]
trans-nonachlor[a]	NQ	NQ	NQ	0.99	1.2	1.2	0.91	1.1	ND	1.1	ND	0.80	0.83	ND	ND	0.92	0.82	ND	1.2	ND	ND	1.0±0.2[c]
Simazine[b]	14	6.5	22	18	18	27	14	14	10	18	26	19	24	20	20	16	17	14	ND	ND	ND	18±5[c]
Trifluralin[a]	NQ	NQ	0.52	0.53	0.19	0.37	0.37	0.27	0.23	0.22	0.41	0.37	0.31	0.31	0.25	0.14	0.16	0.18	0.23	ND	0.12	0.3±0.1[c]

ND = not detected. NQ = detected but not quantified.
[a]Results from GC/NCI-MS analysis; mass spectral confirmation criteria could not be met in NCI-MS for diazinon.
[b]Results from GC/ITMS analysis.
[c]Results in bold text not included in average.

TABLE 4

Concentrations of pesticides in water samples (ng/l) collected on the listed dates in 1997 and the overall averages and standard deviations (SD) from the Choptank River site.

Pesticide	5/27	6/6	6/10	6/19	6/25	7/2	7/17	7/29	8/12	8/27	9/9	10/16	11/11	Average ±SD
Atrazine[b]	180	306	199	254	233	363	432	375	241	330	137	76	57	245 ± 115
CIAT[b]	65	64	44	38	56	53	59	54	52	58	54	35	36	51 ± 10
trans-chlordane[a]	ND	0.01	0.03	0.16	0.04	0.08	0.34	0.01	0.39	0.03	0.07	0.03	0.03	0.1 ± 0.1
Chlorothalonil[a]	ND	ND	ND	ND	ND	ND	2.4	44	18[b]	9.6	235	0.97	ND	variable
Chlorpyrifos[a]	1.2	0.41	0.41	0.53	0.23	0.34	0.72	0.34	1.2	0.32	0.27	0.27	0.19	0.5 ± 0.3
Cyanazine[b]	ND	43	32	21	60	30	34	32	36	28	24	4.9	ND	31 ± 14[c]
Diazinon[b]	ND	ND	ND	ND	ND	ND	11	10	10	13	ND	ND	ND	—
Endosulfan I[a]	0.32	0.26	0.32	0.18	0.15	0.26	0.42	0.31	2.7	0.40	44	0.90	0.91	0.4 ± 0.3[c]
Endosulfan II[a]	0.50	0.39	0.40	0.19	0.15	0.26	0.38	0.48	5.0	0.84	225	0.21	1.4	np[c]0.5 ± 0.4[c]
Endosulfan sulfate[a]	0.31	0.34	0.36	0.19	0.17	0.21	0.33	0.30	3.6	0.40	26	0.18	0.42	0.29 ± 0.09[c]
α-HCH[a]	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	—
γ-HCH[a]	0.48	0.45	0.48	0.41	0.43	0.38	0.32	0.31	0.47	0.21	0.16	0.17	0.21	0.3 ± 0.1[c]
Metolachlor[b]	48	58	31	27	14	38	20	10	3.7	7.4	3.5	0.50	2.3	20 ± 19[c]
trans-nonachlor[a]	0.50	0.18	ND	0.32	ND	0.45	ND	ND	1.3	ND	ND	ND	ND	0.6 ± 0.4[c]
Pendimethalin[b]	ND	ND	ND	ND	ND	ND	ND	ND	18	ND	ND	ND	ND	—
Simazine[b]	84	188	128	102	127	140	168	333	86	102	56	29	24	121 ± 80[c]
Trifluralin[a]	0.60	0.15	0.24	0.49	0.20	0.35	0.33	0.06	0.44	ND	0.06	0.40	ND	0.3 ± 0.2[c]

ND = not detected. NQ = detected but not quantified.
[a]Results from GC/NCI-MS analysis.
[b]Results from GC/ITMS analysis.
[c]Results in bold text not included in average.

Atrazine

Atrazine is a widely used pre-emergent herbicide commonly applied during the planting of corn, during the first week of May (Pait et al., 1992), and CIAT is formed from microbial degradation of atrazine in the soil (Torrents et al., 1997). Trends in atrazine and CIAT concentrations are presented in Fig. 2. During the February–November 1997 sampling period, concentrations of atrazine and CIAT ranged from 25 to 78 ng/l and 17 to 56 ng/l, respectively in the Patuxent River samples, and from 57 to 432 ng/l and 24 to 65 ng/l, respectively, in the Choptank River samples. In comparison with previous years, concentrations of atrazine in Patuxent River samples taken from the mouth of the river between April and June 1994 ranged from below detection limits to 25 ng/l (Harman, 1996). In 1995, Patuxent River water samples collected from a site 10 km north of the 1997 Gatton Bar site had atrazine and CIAT concentrations which ranged from 8–126 ng/l and 7–40 ng/l, respectively, in April and May (Harman, 1996).

In general, atrazine water concentrations are influenced mainly by rainfall after applications (Glotfelty et al., 1984). Unlike the 1997 concentrations, which peaked in mid-June and early July, the 1994 and 1995 water concentrations of atrazine and CIAT reached maximum levels in mid-May. However, 1997 was unusual in that only three significant rain events (> 1 cm) occurred between 1 May and 1 July, whereas 10 events took place during the same time period in 1995 (Harman, 1996). The lack of rain may have acted to delay run-off of atrazine and CIAT from the soil until mid-June and July.

In comparing the two rivers, higher concentrations of atrazine were observed in the Choptank than in the Patuxent, which were most likely a result of greater usage and/or a closer proximity of the sampling site to farms in that watershed. Concentrations of atrazine in the Choptank River peaked at approximately the same time as in the Patuxent, however, background levels prior to the agricultural season were not determined in the Choptank River. Decreased atrazine and CIAT concentrations in November suggest that a longer sampling period in the Choptank River may have shown water concentrations similar to those seen in the Patuxent River in the periods prior to application.

Metolachlor

Metolachlor has recently surpassed atrazine as the most heavily applied pesticide in the Chesapeake Bay region with nearly 600000 kg applied in 1991 (Maryland Dept. of Agriculture, 1993). Metolachlor is a pre-emergent herbicide applied to corn, often mixed with atrazine, in early May, and to soybeans in late May to June depending on weather conditions and farmer crop rotation. As seen for the other herbicides, the Patuxent River water samples had lower concentrations than the Choptank River samples (Table 3 Table 4) with maximum concentrations of 8.7 ng/l in the Patuxent in late May, and 58 ng/l in the Choptank in early June. Metolachlor was observed to decrease in a nearly linear fashion in both rivers until late July or August when 'baseline' levels of ~3 ng/l were maintained in both Rivers.

Simazine and cyanazine

The analytical results for the triazine herbicides, simazine and cyanazine in the water samples were not as consistent between the two rivers as in the case of atrazine and metolachlor. The trend for simazine in the

Choptank samples was similar to that for atrazine in both rivers (Fig. 2), but in the Patuxent samples, simazine concentrations remained consistent at 18 ± 5 ng/l from 13 February to 26 August (Table 3). In the Choptank River, simazine concentrations tracked atrazine in the water with simazine levels 2.3 ± 0.6 times lower than atrazine throughout the 27 May-11 November sampling period. However, the atrazine/simazine ratio was 2.1 ± 0.1 in the Patuxent samples from 13 February-8 May and it rose to 3.2 ± 0.7 in the samples after 8 May (when atrazine is traditionally applied to cornfields) until 26 August. Perhaps simazine was used sparingly by farmers in the Patuxent River watershed in 1997 and a 'baseline' level was observed, but a number of other possible explanations also exist.

The concentrations of cyanazine in the Choptank River water remained fairly steady at 34 ± 11 ng/l for the 6 June-9 September samples (Table 4). In the

Patuxent River, cyanazine concentrations varied widely and suddenly over time from below the LOD to 89 ng/l on 14 April (Table 3). The rapidity of change in the concentrations indicates that cyanazine does not persist in surface waters. The soil dissipation half-life for cyanazine is typically only 14 days (Hornsby et al., 1996) and on the basis of these results, it appears that fairly uniform amounts of cyanazine were applied at regular intervals during the summer months in the Choptank River watershed because cyanazine would have dissipated rapidly, as observed in the Patuxent River, if no new applications took place.

Other pesticides in water

As a further comparison of results from the Patuxent and Choptank Rivers, Fig. 3 displays the trends in water concentrations for the insecticides, chlorpyrifos and diazinon, and the fungicide, chlorothalonil. It should be noted that there are differences in scales of
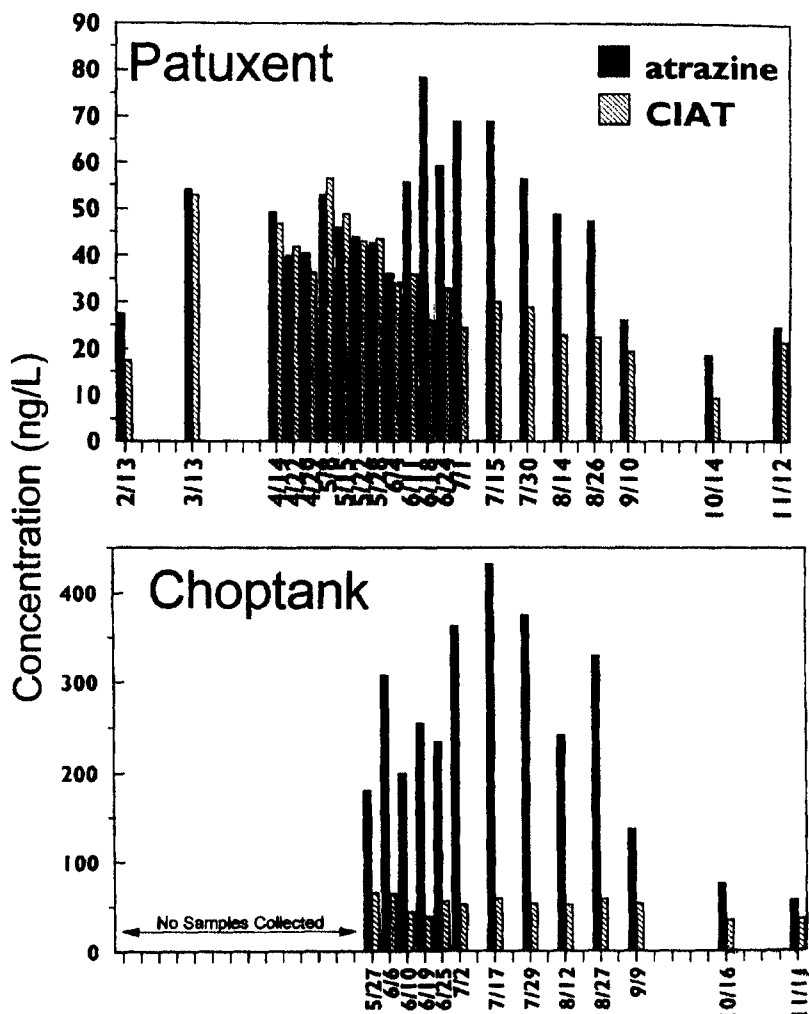

Fig. 2 Trend of results for atrazine and CIAT determined in water samples from the Patuxent and Choptank Rivers during 1997.

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concentrations and sampling periods between the Patuxent and Choptank River data shown in Fig. 3. Overall, the concentrations of these three compounds were much lower than the herbicides. The difference in concentration levels between the two groups is expected as total usage in the Chesapeake Bay watershed of these pesticides is small compared with the herbicides (Pait et al., 1992).

Chlorpyrifos is an organophosphate (OP) insecticide that is widely used on a number of crops including corn and soybeans, and in residential and urban areas as a termiticide and for general insect control (Racke, 1993). Chlorpyrifos levels in the Patuxent River were highest in the spring (maximum, 3.1 ng/l on 29 April) declining throughout the summer to approximately 1.0 ng/l with the exception of one peak in the 24 June sample. This is the same trend that was seen at the mouth of the Patuxent River during 1995 by Harman (1996) and in the Chesapeake Bay mainstem by McConnell et al. (1997). The peak concentration observed in the Patuxent does not coincide with peak usage during late May and August, and the reason for this trend is still under investigation. In the Choptank, because of the shorter sampling period, the trend for chlorpyrifos in the early spring was impossible to observe. Overall, concentrations were lower in the

Choptank than in the Patuxent (0.5 ± 0.3 ng/l vs 1.5 ± 0.8 ng/l) with two peaks over 1.0 ng/l at the end of May and the middle of August, presumably occurring soon after agricultural applications.

Chlorothalonil is a fungicide that is registered for use on a number of vegetable crops (EPA, 1997) and may be applied several times during the season depending on weather conditions. Unlike the herbicides and chlorpyrifos, chlorothalonil levels remained very low (<0.7 ng/l) or undetected at both locations until the months of July and August (Fig. 3). The maximum chlorothalonil concentration was 159 ng/l in the Patuxent River at the end of July and 236 ng/l in the Choptank River in mid-August. These spikes coincided with predicted use patterns for chlorothalonil on vegetables such as tomatoes. The low levels during the remainder of the sampling period suggest that this compound has a short half-life in surface water. This observation is supported by a recent review on the environmental fate and effects of chlorothalonil which reports half-life values as low as 4.3 h in fresh water, with microbial activity constituting a major breakdown process (Caux et al., 1996).

Diazinon is another widely used OP insecticide applied to control grubs in soil and pests of vegetables, fruits, and tobacco. As with chlorothalonil, levels in

Patuxent River Water Results

Choptank River Water Results
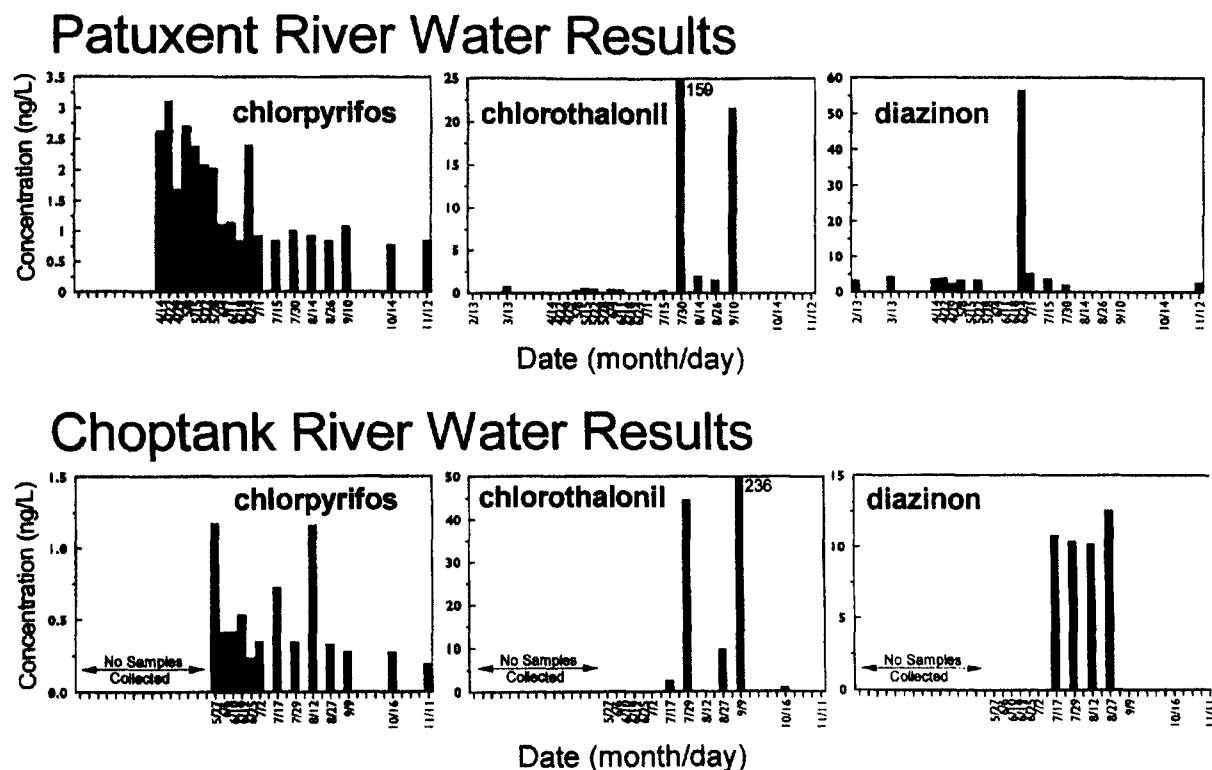

Date (month/day)

Fig. 3 Trend of results for chlorpyrifos, chlorothalonil, and diazinon determined in water samples from the Patuxent and Choptank Rivers during 1997.

both rivers were low (<4.2 ng/l) or undetectable until the late summer (Fig. 3). A large spike in concentration was observed in the 24 June Patuxent River sample (56 ng/l) followed by much lower concentrations <5.1 ng/l for the remainder of the summer. In the Choptank, diazinon was below the LOD until mid-July when a sustained spike of 10–13 ng/l was observed through the end of August. Again, these spikes coincided with expected use patterns for vegetable production and also suggest a limited lifetime in surface waters. The observed peaks in chlorpyrifos, diazinon and chlorothalonil, however, occurred independently of rainfall events which indicates that other processes, such as atmospheric deposition rather than run-off, may be an important transport pathway for these currently used pesticides (McConnell et al., 1997).

Persistent, banned OC insecticides, *trans*-nonachlor, *cis*-chlordane, and the breakdown product of p,p'-DDT, p,p'-DDE, were also detected in the water at consistently low levels throughout the year (Table 3 and Table 4). As with all insecticides determined, concentrations of OC insecticides in the Choptank River were lower than those in the Patuxent. Also, no large spikes in the concentrations of these analytes occurred in the samples during the summer. Furthermore, the trend in the early spring which occurred for chlorpyrifos and endosulfans was also missing in the case of these OC insecticides. These trends are as one would expect for prohibited pesticides which do not have peak application periods.

The sparsely used seed protectant, γ-hexachlorocyclohexane (HCH), also known as lindane, and one of its co-formulants, α-HCH, were also detected in water samples, but the results were inconclusive and further information is needed to warrant discussion. Trifluralin, endosulfan I and II were determined in the water and oyster samples and a more complete discussion is presented in the following section.

Oyster results

The results for oysters collected in the study from the Patuxent and Choptank Rivers are presented in Table 5 and Table 6. Many of the same insecticides (*trans*-chlordane, *trans*-nonachlor, p,p'-DDE, o,p'-DDT, and α- and γ-HCH), which were determined in this study, have previously been found by the MWP in oysters collected from the same or nearby sites within the standard deviations of the average values reported here since 1986 (NOAA, 1997). The banned OC pesticide p,p'-DDT, which has also been found in oysters by the MWP, was confirmed by mass spectrometric detection but quantitation was highly variable and concentration values could not be assigned. The current-use pesticides, chlorpyrifos and endosulfan I and II, have been monitored by the MWP since 1995, and in that time, only one sample from the Hog Point site at the mouth of the Patuxent River contained detectable levels of endosulfan II.

Compounds determined in this study which were not previously detected in these two tributaries by the MWP included chlorpyrifos, trifluralin, endosulfan I, endosulfan sulfate, and *cis*-chlordane. None of the heavily used triazine and acetanilide herbicides were detected in the oysters despite their high concentrations in the water. This was not surprising, however, due to the relatively polar nature of these chemicals (log K_{ow} <4), and since previous MWP-sponsored studies did not detect these herbicides in oysters (O'Connor, T. P., pers. comm., 1997).

Trifluralin

Figure 4 displays the oyster and water results for the dinitroaniline herbicide, trifluralin, which was the only herbicide detected in the oysters. Of all the analytes determined in the water, only trifluralin was found to have similar concentrations in samples from both rivers (0.30 ± 0.12 ng/l in the Patuxent samples and 0.30 ± 0.18 ng/l in the Choptank samples for an overall

TABLE 5

Concentrations of pesticides in oyster samples (ng/g), wet weight, collected on the listed dates in 1997 and overall averages and standard deviations (SD) from the Patuxent River site.

Pesticide	2/13	3/13	4/14	4/29	5/8	5/15	5/22	5/29	6/4	6/11	6/18	6/24	7/1	7/15	7/30	8/14	8/26	9/10	10/14	11/12	Average ±SD
cis-chlordane[a]	0.23	0.37	0.51	0.30	0.39	0.16	0.40	0.41	0.45	0.42	0.42	0.51	0.45	0.39	0.35	0.37	0.28	0.49	0.39	0.40	0.38±0.09
trans-chlordane[a]	0.23	0.37	0.42	0.31	0.39	0.35	0.50	0.45	0.51	0.47	0.38	0.63	0.58	0.41	0.33	0.18	0.20	0.27	0.26	0.37	0.38±0.12
Chlorpyrifos[a]	0.23	0.42	0.41	0.33	0.36	0.19	0.35	0.36	0.34	0.21	0.17	0.36	0.30	0.27	0.30	0.20	0.16	0.16	0.16	0.23	0.28±0.09
p,p'-DDE[a]	0.56	0.77	0.79	0.60	0.73	0.89	1.2	0.96	1.2	1.1	0.72	1.2	1.1	1.0	0.87	0.52	0.47	0.60	0.64	0.74	0.83±0.24
o,p'-DDT[a]	ND	ND	0.36	0.36	0.20	0.15	0.22	0.14	0.42	0.30	0.13	0.48	0.46	0.35	0.66	0.21	1.2	0.61	0.12	0.44	0.36±0.26[b]
Diazinon[a]	2.1	2.9	0.95	0.81	0.88	2.3	2.0	2.0	1.6	2.0	4.0	2.0	4.4	5.3	1.7	0.88	0.90	0.82	ND	0.88	2.0±1.3
Endosulfan I[a]	0.076	0.14	0.19	0.16	0.21	0.15	0.17	0.16	0.22	0.17	0.13	0.23	0.15	0.36	0.36	0.14	0.15	0.16	0.085	0.17	0.18±0.07
Endosulfan II[a]	0.16	0.14	0.31	0.44	0.11	0.084	0.090	0.056	0.12	0.069	0.047	0.063	0.033	0.087	0.39	0.074	0.072	0.075	0.069	0.093	0.13±0.11
Endosulfan sulfate[a]	0.34	0.47	0.62	0.68	0.38	0.36	0.43	0.34	0.39	0.37	0.26	0.36	0.33	0.29	0.70	0.18	0.20	0.24	0.15	0.26	0.37±0.15
α-HCH[a]	0.048	0.676	0.14	0.079	0.094	0.077	0.22	0.10	0.26	0.49	0.25	0.80	0.79	0.072	0.050	0.061	0.042	0.039	0.031	0.061	variable
γ-HCH[a]	0.12	0.54	0.17	0.13	0.14	0.15	0.17	0.18	0.15	0.11	0.14	0.19	0.17	0.25	0.15	0.073	0.084	0.072	0.056	0.096	0.16±0.10
trans-nonachlor[a]	0.27	0.41	0.41	0.31	0.38	0.36	0.45	0.41	0.48	0.44	0.39	0.57	0.54	0.46	0.41	0.32	0.27	0.34	0.33	0.37	0.40±0.08
Trifluralin[a]	0.007	0.016	0.090	0.065	0.073	0.049	0.084	0.069	0.14	0.12	0.081	0.30	0.16	0.086	0.042	0.011	0.015	0.012	0.009	0.022	variable

ND = not detected.
[a]Results from GC/NCI-MS analysis; mass spectral confirmation criteria could not be met for diazinon.
[b]Results in bold text not included in average.

TABLE 6

Concentrations of pesticides in oyster samples (ng/g), wet weight, collected on the listed dates in 1997and overall averages and standard deviations (SD) from the Choptank River site.

Pesticide	5/27	6/6	6/10	6/19	6/25	7/2	7/17	7/29	8/12	8/27	9/9	10/16	11/11	Average ± SD
cis-chlordane[a]	3.5	1.3	3.3	1.8	1.1	3.9	1.4	1.2	1.9	0.82	1.0	1.1	0.87	1.8 ± 1.1
trans-chlordane[a]	0.72	0.74	0.61	0.60	0.76	0.47	0.46	0.35	ND	ND	ND	0.52	0.55	0.58 ± 0.13[c]
Chlorpyrifos[a]	0.27	0.38	0.20	0.18	0.25	0.15	0.14	0.11	0.095	0.13	0.13	0.23	0.22	0.19 ± 0.08
p,p′-DDE[b]	1.2	1.0	1.7	0.57	0.90	1.1	0.72	0.81	0.60	0.36	0.52	1.2	1.7	0.95 ± 0.42
o,p′-DDT[a]	0.39	0.61	0.40	0.36	0.34	0.33	0.40	0.33	0.14	0.25	0.19	0.33	0.20	0.33 ± 0.12
Diazinon[a]	0.95	0.98	0.49	0.43	0.33	0.27	0.39	0.26	0.17	0.21	0.20	0.30	0.30	0.41 ± 0.26
α-HCH[a]	0.44	0.42	0.79	0.18	0.12	0.27	0.38	0.043	0.099	0.037	0.20	0.078	0.14	0.24 ± 0.21
γ-HCH[a]	0.44	0.18	0.20	0.25	0.14	0.081	0.074	0.067	0.024	0.047	0.054	0.16	0.098	0.14 ± 0.11
trans-nonachlor[a]	0.58	0.64	0.72	0.60	0.74	0.68	0.48	0.44	ND	0.027	ND	0.53	0.39	0.53 ± 0.20[c]
Trifluralin[a]	0.20	0.34	0.35	0.23	0.31	0.19	0.074	0.066	0.020	0.050	0.026	0.042	0.065	0.15 ± 0.12

ND = not detected.
[a] Results from GC/NCI-MS analysis; mass spectral confirmation criteria could not be met for diazinon.
[b] Results from GC/ITMS analysis.
[c] Results in bold text not included in average.

average of 0.30 ± 0.14 ng/l). The solubility of trifluralin in water at 25°C is ≈ 0.5 mg/l and the log K_{ow} is ≈ 4.8 (Hornsby et al., 1996). As shown in Fig. 4, no temporal trend in trifluralin concentration was observed in the water samples, but the herbicide levels increased to a maximum in oysters during June and early July. This time period would generally correspond with a seasonal rise in percent lipid content as oysters
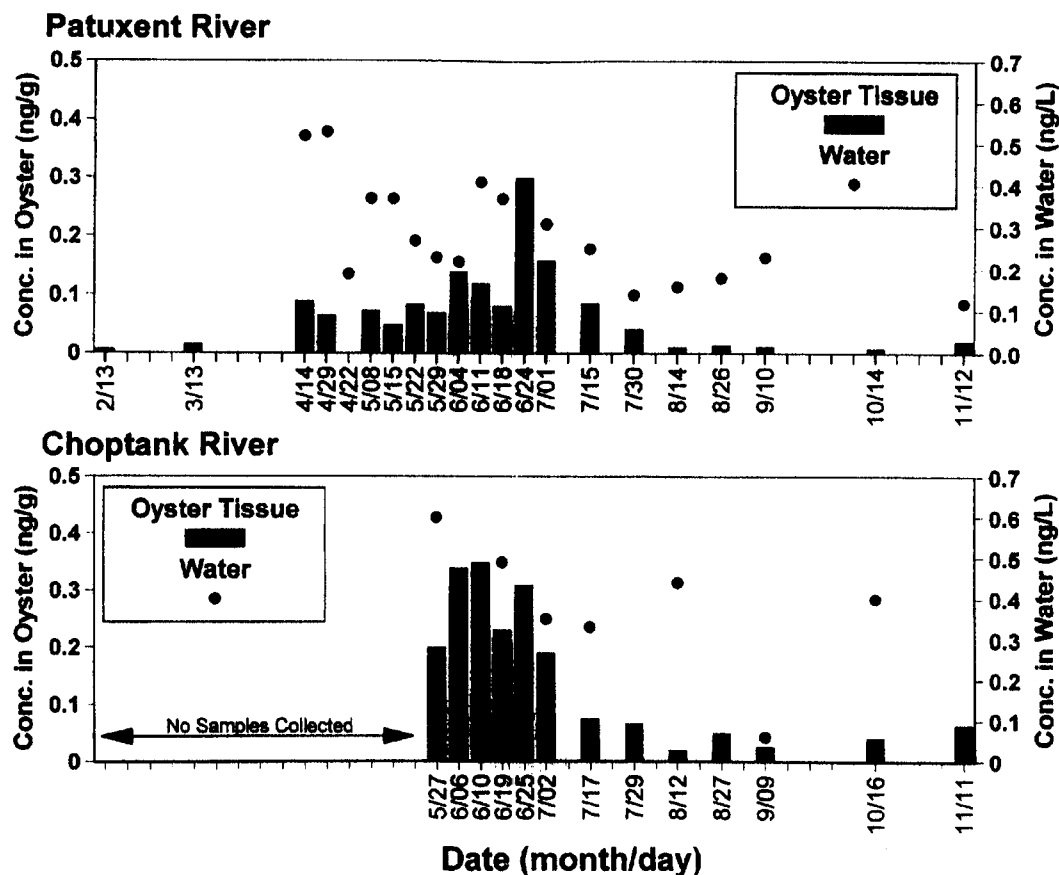

Fig. 4 Trend of results for trifluralin in the water and oyster samples from the Patuxent and Choptank Rivers over the course of the study.

accumulate glycogen prior to spawning. This time frame also corresponds with the time of year trifluralin is most commonly applied to crops (Pait et al., 1992), and it appears that trifluralin accumulated in the oyster tissue soon after application and then degraded fairly rapidly in oysters. This suggests that this class of chemicals may be metabolized and/or excreted by oysters and therefore, does not pose a persistence problem, however, further study would be necessary to verify this conclusion.
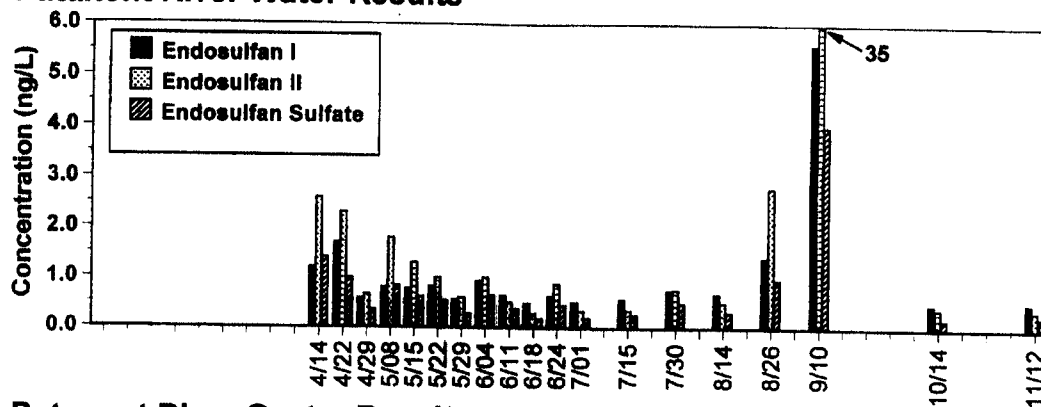
Endosulfans

Endosulfan is an insecticide commonly used on vegetables in the mid-Atlantic region, and applied formulations consist of a mixture of ≈7:3 endosulfan I:endosulfan II (Rice et al., 1997). Endosulfan has been shown to be very toxic to fish and other aquatic organisms (Schimmel et al., 1977). Endosulfan I and II have distinct physicochemical properties, whereby endosulfan I has a higher vapor pressure and lower solubility in water than endosulfan II (Cotham and Bidleman, 1989; Schmidt et al., 1997). Endosulfan

sulfate is a major soil degradation product of endosulfans I and II which is transported by run-off and leaching to adjacent waters (Pesticide Manual, 1983).

While all three endosulfan compounds were observed in water from both the Patuxent and Choptank Rivers, only the oysters from the Patuxent River contained detectable levels of these analytes. Figure 5 presents the water and oyster analytical results for endosulfan I, endosulfan II, and endosulfan sulfate for the Patuxent River. In the water, higher than average concentrations for all three compounds were observed in April as was seen for chlorpyrifos (Fig. 3). After this initial trend, the concentrations remained rather consistent from 29 April–14 August. Endosulfan II had the highest concentration in the water, even though approximately half as much endosulfan II is present in the pesticide formulation (Rice et al., 1997). The reasons for this are of great interest and are being investigated further.

There was a peak in the water concentrations in the late summer for all three endosulfan compounds in both rivers, presumably due to applications in the region. Endosulfan II increased to as much as 35 ng/l
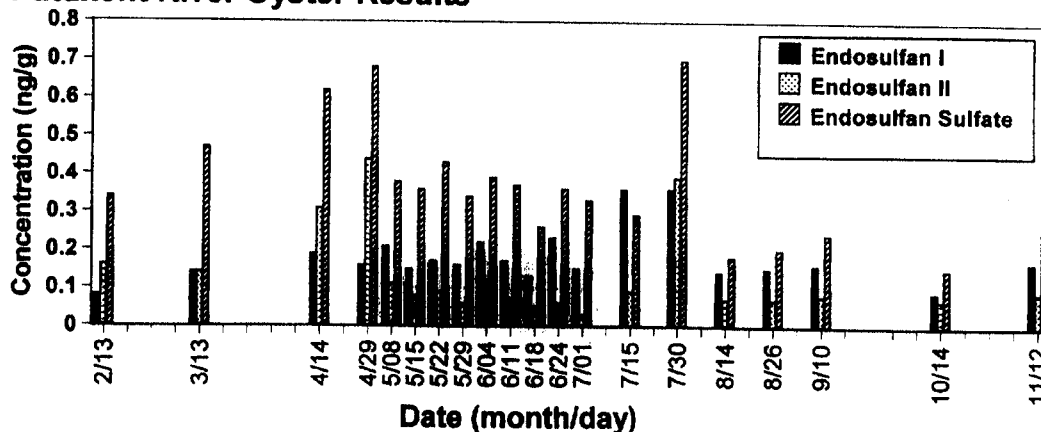

Fig. 5 Trend of results for endosulfans in the Patuxent River water and oyster samples over the course of the study.

in the 10 September sample (Table 3) in the Patuxent River and 226 ng/l in the Choptank River on 9 September (Table 4). This concentration exceeds the EPA's freshwater water criteria of 56 ng/l for endosulfan (EPA, 1986). Otherwise, the average levels in the Choptank were lower than in the Patuxent, and the lower concentrations (below LOD) in the oysters from the Choptank River demonstrated a long-term correlation between the levels in the water and oysters.

The concentration of endosulfans in Patuxent River oysters remained relatively constant over the sampling period. Unlike the case for the water, endosulfan sulfate consistently had the highest concentration in oysters averaging 0.37 ± 0.15 ng/g, followed by endosulfan I at 0.18 ± 0.07 ng/g and endosulfan II at 0.13 ± 0.11 ng/g. There was no apparent short-term correlation between the measured dissolved phase water concentrations and the levels in oyster tissue. The pesticide levels in the oysters appeared to remain constant despite the sudden increase in water concentrations in September. Since only one sample was collected at each site in September, not enough information was obtained to draw accurate conclusions about the correlations between water and oyster results. More intensive data collection is required to determine the most important factors involved in the uptake of endosulfan by oysters.

Conclusions

The results of this study demonstrated that 18 of the targeted compounds were detected in the water samples and 13 in oyster tissue. Of those detected, several currently used pesticides were found in water including atrazine, chlorothalonil, chlorpyrifos, CIAT, cyanazine, diazinon, endosulfans, lindane, metolachlor, pendimethalin, simazine, and trifluralin with the highest concentrations found for the corn herbicide atrazine and its degradation product CIAT. In the case of oysters, only chlorpyrifos, endosulfans and trifluralin and possibly diazinon were detected. Only trifluralin increased in concentration in oyster tissue during the 1997 agricultural season, and its levels subsided quickly prior to September. In the case of chlorpyrifos, the water and oyster concentrations were 3 to 5 orders of magnitude lower than the LC_{50} for fish and oysters (Serrano et al., 1995). Endosulfan peak concentration in the Choptank River water in September, however, may have approached the LC_{50} for some aquatic organisms (Schimmel et al., 1977). The presence of current-use pesticides, particularly endosulfans and chlorpyrifos, in the water and oysters many months after agricultural applications indicates that their persistence in the environment warrants further monitoring. Oysters depurate contaminants on a time scale of weeks to months so they may lag behind the response of the water concentrations (Serrano et al., 1997) A future report will incorporate the results of particle phase water concentration and sediment samples collected at the same times during this project.

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CORRIGENDUM

S.J. Lehotay, J.A. Harman-Fetcho, and L.L. McConnell, 1998. "Agricultural Pesticide Residues in Oysters and Water from Two Tributaries of the Cheaspeake Bay", *Marine Poll. Bull.* **37(1-2), 32–44**

The reported concentrations of endosulfans and chlorothalonil in the water samples collected during the August–September 1997 time frame are incorrect. The high concentrations of these pesticides in the water were due to contamination from a filtering apparatus which was also used in other studies in the laboratory. We very much regret this mistake and have taken actions to avoid cross-contamination of samples by purchasing a separate filtering apparatus for trace applications only. Results for all other pesticides in water, all oyster samples, and chlorothalonil and endosulfans during other months were not affected by the contamination.